

Geometrically induced transitions between equilibrium crystal shapes

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Abstract. Using results of the anisotropic surface tension of the two-dimensional Ising model on a square lattice, the exact location of a new class of transition between different cluster shapes is obtained at all temperatures below T_c , in systems with conserved total magnetization and periodic boundary conditions. We study the general cases of anisotropic couplings and rectangular system geometries. Monte Carlo simulations confirm our findings. Finite-size effects relevant to the simulations are also analysed. Generalizations to other system topologies, and the saddle point associated with the transitions, are discussed.

1. Introduction

The subject of equilibrium crystal shape has a long history (Wulff 1901, Herring 1953). Due to advances in both theoretical understanding in related phase transitions and in experimental techniques, it has received considerable recent attention (Wortis 1988, Zia 1988).

The problem studied traditionally deals with infinite systems, in which the crystal is an isolated object. Considerations of the boundary never enter, except in the case of semi-infinite systems in which the crystal is an object attached to one (Winterbottom 1967) or more (Zia *et al* 1988) boundaries. In other words, the crystal volume is negligible compared with the surrounding medium. Not surprisingly, if the crystal occupies a finite fraction of the system, we should expect non-trivial effects due to the boundaries, which carry information about the geometry and topology of the system. In particular, transitions between a 'localized' cluster and an 'extended' one become possible, since the system will, in equilibrium, favour the crystal shape with the lowest total free energy.

In this paper, we explore such transitions, both analytically and by simulations, in a simple system—the two-dimensional (2D) Ising model on a square lattice. Of course, to have a droplet, we must work with fixed total magnetization, below the critical temperature T_c . Note that these transitions occur *within* the co-existence curve. Key to the results is the knowledge of the exact anisotropic surface tension and equilibrium crystal shape for this system.

The exact location of the transition at all temperature is given in section 2, explicitly for the equal-coupling case, and implicitly for the case of anisotropic coupling and system shape. Along with a detailed discussion of the finite-size effects (section 3), Monte Carlo simulation results, for a limited range of temperature, are presented (section 4) which confirm the exact results. The dependence of such morphological

transitions on the topology of the system, as well as the associated saddle point, are discussed in section 5.

2. Exact results

We begin by considering the thermodynamic limit of the two-dimensional Ising model on a square lattice, with periodic boundary conditions (PBC), for which extensive exact results exist. We will use the spin language, with $J > 0$ being the isotropic, ferromagnetic nearest-neighbour coupling. For temperatures T below the critical one T_c , the spontaneous magnetization $M(T)$ is a celebrated function (Onsager 1944, Yang 1952). If we *constrain* the magnetization $\bar{\phi}$ to lie within the range $(-M, +M)$, then the system phase separates into two regions with volume fractions appropriate to the Maxwell construction. Thus, if $\bar{\phi} = 0$, the two regions will each have half the volume of the total system. Since we have a square system with PBC, it is clear from symmetry alone that each region must be just a strip, aligned with one of the axes (figure 1(a)). If we vary $\bar{\phi}$ toward, say, $-M$, then the width of the $+M$ strip must decrease accordingly. However, if $\bar{\phi}$ is very near $-M$, we expect the $+M$ region to assume a droplet form (figure 1(b)), since the interface between the two regions will be 'shorter' than the strip case, so that it is energetically much more favourable. For $\bar{\phi}$ somewhere between $-M$ and 0, the droplet-strip transition occurs.

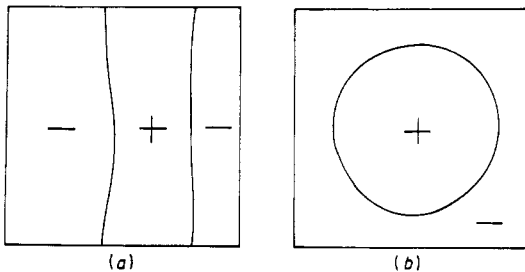


Figure 1. Schematic illustrations of a snapshot of the (a) strip phase, and the (b) droplet phase.

Crucial to the droplet-strip transformation are the surface tension (free energy per unit length) σ_0 of a planar interface aligned with a lattice axis and the total surface free energy associated with a droplet. For the latter, both the anisotropic surface tension $\sigma(\hat{n})$, for an interface with normal \hat{n} , as well as the equilibrium droplet shape are needed. Fortunately, all of these quantities are known exactly for our model (Zia and Avron 1982).

In order to identify the critical magnetization $\bar{\phi}_c(T)$ at which the droplet-strip transition occurs, we simply compare the free energies of the two configurations. First, let us use a more convenient parametrization: the fractional magnetization

$$f(\bar{\phi}, T) \equiv \frac{\bar{\phi} + M(T)}{2M(T)} \quad (2.1)$$

so that fL^2 is just the volume of the $+M$ phase in our $L \times L$ system.

The free energy associated with the bulk phases is, in the $L \rightarrow \infty$ limit, *independent* of the shape of the regions. Thus, the energetics are controlled purely by Σ , the (total)

surface free energies, which are shape dependent. For a strip, which has two flat interfaces of length L , we have

$$\Sigma_S = 2\sigma_0 L. \quad (2.2)$$

Note that this is independent of the volume of the strip, which fixes the width rather than the length of the $+M$ region.

For a droplet, whose shape is neither square nor circular for general T , the total surface energy Σ_D can be obtained only through the Wulff's construction (Zia and Avron 1982):

$$\Sigma_D = 2\sqrt{WV_D} \quad (2.3)$$

where W is the volume bounded by the Wulff's plot and V_D is the volume of the droplet. Since the latter is just fL^2 , we see immediately the cause of the droplet-strip transition. For small f , (2.3) is favourable. When f reaches

$$f_c = \frac{\sigma_0^2}{W} \quad (2.4)$$

Σ_S is lower and the strip configuration wins. Note that this transition is not a finite size effect, surviving in the thermodynamic limit.

Generalization of equation (2.4) to arbitrary dimensions d is immediate, since (2.3) is known (Zia and Avron 1982) for all d . We simply quote the result:

$$f_c = \left[\frac{(2\sigma_0/d)^d}{W} \right]^{1/(d-1)} \quad (2.5)$$

which is valid for an L^d system with periodic boundary conditions (a hyper-torus).

As T varies, so do σ_0 and W , giving us $f_c(T)$ as a function of T . This result reduces to purely geometric quantities in the limits $T=0$ and T_c , where we know that the droplet shape in 2D is a square and a circle, respectively. In the former case, the 'length' from the centre to the edge (of the square Wulff shape) is $\sigma_0 (=2J)$, so that $f_c(0) = \frac{1}{4}$. In the latter case, the 'radius' of the Wulff volume is σ_0 , giving us $f_c(T_c) = 1/\pi$. For $d > 2$, these limits are $f_c(0) = d^{-d/(d-1)}$ and $f_c(T_c) = (2/d)[\Gamma(d/2)/\pi^{d/2}]^{1/(d-1)}$. It is amusing to note that as $d \rightarrow \infty$, $f_c \rightarrow 0$: there a slab with two $(d-1)$ -dimensional interfaces always has a lower free energy, and is thus the equilibrium configuration.

For arbitrary $T < T_c$, not much is known exactly in general dimensions. Returning to $d = 2$, the exact σ_0 is provided by a simple formula (Onsager 1944):

$$\frac{\sigma_0(T)}{J} = 2 + \frac{1}{\beta J} \ln \tanh \beta J \quad (2.6)$$

where $\beta \equiv 1/k_B T$. Although the equation describing the Wulff shape is also very simple (Zia and Avron 1982), we are not able to obtain a closed form for its volume:

$$W = 4\beta^{-2} \int_0^{\beta\sigma_0} dx \cosh^{-1} \left[\frac{(\cosh 2\beta J)^2}{\sinh 2\beta J} - \cosh x \right]. \quad (2.7)$$

This integral is computed numerically and the resultant phase diagram is shown in figure 2.

More generally, we can consider systems with anisotropic couplings, i.e. $J_x \neq J_y$, and/or rectangular geometry, i.e. $L_x \neq L_y$. The phase diagram will be modified, while some new features emerge. Although the exact W can be found (by numerical integration), since the surface tension and equilibrium shape for the unequal coupling case

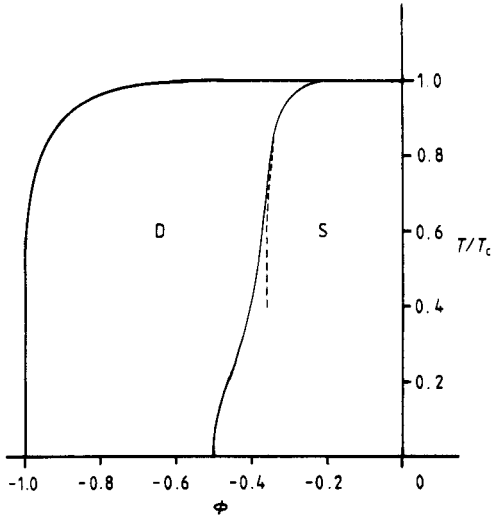


Figure 2. Phase diagram of the equilibrium crystal-shape transition in an $L \times L$ 2D Ising model on a square lattice, with equal coupling. The bold full curve is the coexistence curve, the fine one is the exact location of the transition between droplet (D) and strip (S) phase. The broken curve is the approximation $f_c \approx 1/\pi$.

are available in closed forms (Zia and Avron 1982), we will limit our discussions here only to the limits $T = 0$ and $T = T_c$. In these limits, the modifications can be understood simply, while no essential new physics can be learnt by studying the general phase boundary.

Let us define ratios $\rho_J \equiv J_y/J_x$, $\rho_\sigma \equiv \sigma_y/\sigma_x$ and $\rho_L \equiv L_y/L_x$, where σ_x and σ_y stand for $\sigma(\hat{x})$ and $\sigma(\hat{y})$, respectively. In the low temperature limit, $\rho_\sigma \rightarrow \rho_J$, while near T_c , $\rho_\sigma = \sinh 2\beta_c J_y$ (Zia and Avron 1982), where β_c is determined via the transcendental equation

$$\sinh(2\beta_c J_x) \sinh(2\beta_c J_x \rho_J) = 1.$$

Now for given ρ_σ and ρ_L , the strip may align either along \hat{x} or \hat{y} , depending on whether $\sigma_x L_y$ or $\sigma_y L_x$ is smaller. Denoting the larger (smaller) of ρ_σ and ρ_L by $\rho_>$ ($\rho_<$), we have $\Sigma_S = 2\rho_< \sigma_x L_x$.

For the droplet, we use equation (2.3). Thus, near $T = 0$, where the shape is just a rectangle, we have $\Sigma_D = 2\sqrt{4J_x J_y f L_x L_y}$. Similarly, near T_c , $\Sigma_D = 2\sqrt{\pi \sigma_x \sigma_y (f L_x L_y)}$. In either case, we can write these as $\Sigma_D = 2\sqrt{g \rho_> \rho_< f} \sigma_x L_x$, where the geometric factor $g = 4$ or π accordingly.

Equating Σ_S and Σ_D then yields the simple result

$$f_c = \frac{1}{g} \frac{\rho_<}{\rho_>} \tag{2.8}$$

which is always less than the values for the isotropic-square case.

3. Finite-size dependence of f_c

To visualize the droplet-strip transition, and to confirm the exact results of the last section, we study the equilibrium configurations by Monte Carlo method. Since we

are interested only in systems with fixed mean magnetization $\bar{\phi}$, we are seriously limited by slow dynamics and metastability. Thus, we can only extract sensible results from runs of relatively small L . This necessitates the study of finite-size properties of f_c . From now on we will be concerned only with the equal coupling case.

Several sources of finite-size effects can be identified. They arise from:

- (a) entropy terms in Σ associated with the mean position of the cluster;
- (b) differences in the finite-size effects of σ between the strip and the droplet;
- (c) Gibbs–Thomson relation, which describes the modification of the bulk magnetization in the presence of a finite droplet.

First we discuss the effects of the entropies. Under PBC, the random walk associated with the centre of the cluster contributes a term $-k_B T \ln \mathcal{N}$ to Σ , where \mathcal{N} , the degeneracy, is $2L$ for the strip and L^2 for the droplet. This in principle yields a $\ln L/L$ correction to f_c . However, simulation runs in practice are too short to properly sample these entropies. The reason has to do with the cluster diffusivity D being very small. D , defined as the mean square distance travelled per unit time, decreases as a power of the cluster size (Binder and Kalos 1980). For large L , in either the strip or droplet phase, the dominant process contributing to D comes from evaporation and condensation of spins at different places on the interface. This gives $D \sim e^{-8\beta J} L^{-1}$. To sample the entropies by simulation, the number of Monte Carlo steps τ must be sufficiently long that $(D\tau)^{1/2} > cL$, where c is some large number. As an example, taking $c = 10$ and $L = 30$ leads to $\tau > 10^8$ for both the droplet and the strip. This is two to three orders of magnitude longer than our simulations. Therefore, we may neglect the effects of the entropies.

It is more difficult to assess the significance of source (b). It has been well established that for planar interfaces, the leading finite-size correction to σ in 2D is $\ln L/L$ (Privman 1988, Gelfand and Fisher 1988). This applies to the strip phase. Although we expect the same form of correction to hold for the droplet, the computation of the coefficient appears difficult—it is not clear whether the lattice can be ignored. Should the coefficients be different, a $\ln L/L$ term in f_c should be present. However, from the simulation results (see next section), such a term seems to be absent. Since cancellation normally does not occur, this may again be a consequence of improper sampling of capillary wave excitations, which are the sources of the $\ln L/L$ correction; as the interfaces evolve very slowly. In any case, as far as the simulations are concerned, the leading correction in our data appears to be of order $1/L$.

The third source is the Gibbs–Thomson effect, which leads indeed to an $O(1/L)$ correction. Since simulations are done at fairly high T (0.8 and $0.9T_c$), the leading finite-size effects can be deduced by studying a fully isotropic model.

In the range of magnetization of interest (well inside the coexistence region), the droplet radius R is much greater than the bulk correlation length ξ_B which is of the same order as the interface width. When ξ_B is not too small, it is meaningful to consider a continuum model implicitly obtained by some suitable coarse graining on the discrete model. To describe such a model with short-range interaction, we use the standard coarse-grained local magnetization $\phi(x)$ in conjunction with the Landau–Ginzburg free energy:

$$\mathcal{H}\{\phi\} = \int d^d x \left[\frac{1}{2} (\nabla \phi)^2 + U(\phi) \right] \quad (3.1)$$

where the potential U has the usual double-well structure with degenerate minima at $\pm M$ (e.g. the usual ϕ^4 -potential below T_c). To conserve the total magnetization, ϕ

satisfies a global constraint

$$\int d^d x \phi = \bar{\phi} V. \tag{3.2}$$

We assume that the total free energy in either phase can be decomposed into two terms: a bulk term proportional to V , and a surface term proportional to the area of interfaces. Thus, for the droplet and the strip, we have respectively

$$F_D = U(\phi_-) V_D + U(\phi_+)(V - V_D) + \sigma_D A_D \tag{3.3a}$$

$$F_S = U(\pm M) V + 2\sigma_S L. \tag{3.3b}$$

In (3.3b) we take $\pm M$ to be the bulk densities for the strip, because the error is exponentially small. This is not the case for the droplet. Under fixed total magnetization, the equilibrium between a droplet of finite radius R and its surrounding bulk is reached by maintaining a finite ‘chemical potential’ difference between the $+M$ and $-M$ phases in order to balance the ‘pressure’ exerted on the droplet surface. This is achieved by modifying the bulk magnetization: $\phi_{\pm} = \pm M + \delta\phi$, since to lowest order the corrections are the same in both the $+M$ and $-M$ phases. Since the ‘pressure’ is proportional to $1/R$, we expect $\delta\phi \sim 1/R$.

For convenience, we choose $U(\pm M) = 0$. By definition, $dU(\pm M)/d\phi \equiv U'(\pm M) = 0$. We denote

$$\chi^{-1} \equiv U''(M) = U''(-M) \tag{3.4}$$

since U is symmetric in ϕ . Expanding U about $\pm M$, (3.3a) becomes

$$F_D \approx \frac{1}{2\chi} (\delta\phi)^2 L^2 + \sigma_D cR \tag{3.5}$$

where the mean droplet (not necessarily circular) radius is $R \equiv V_D^{1/2}$, and the area $A_D \equiv cR$. The shape factor c is $2\sqrt{\pi}$ for a circular droplet. $\delta\phi$ is determined by minimizing F_D subject to the global constraint (3.2), which yields the correction to the volume fraction

$$\begin{aligned} \frac{R^2}{L^2} &= \frac{\bar{\phi} - \phi_-}{\phi_+ - \phi_-} \\ &= f - \frac{\delta\phi}{2M} + \dots \end{aligned}$$

After eliminating $\delta\phi$ in (3.5), the values of $\delta\phi$ and R at which F_D is a minimum are determined to be

$$\delta\phi = 2M \frac{\xi}{R} + O\left(\frac{1}{R^2}\right) \tag{3.6}$$

$$R = f^{1/2} L - \frac{\xi}{2f} + O\left(\frac{1}{L}\right) \tag{3.7}$$

where $\xi \equiv c\chi\sigma_D/2(2M)^2$ is usually called the capillary length.

Expressing F_D in terms of f , the critical fraction $f_c(L)$ can easily be derived by equating F_D to F_S . Following the above discussion, we may neglect the difference between σ_D and σ_S , and arrive at

$$f_c(L) = \left(\frac{2}{c}\right)^2 + \frac{c\xi}{4L} + O\left(\frac{1}{L^2}\right). \tag{3.8}$$

In the limit of $L \rightarrow \infty$, the droplet shape is circular, we recover the exact result $1/\pi$. For finite L , the droplet shape must reflect the square geometry of the system, as $R/L (\approx 1/\sqrt{\pi})$ is quite large. Allowing for this deviation, $c = 2\sqrt{\pi} + \delta c$, with $\delta c \rightarrow 0$ as $L \rightarrow \infty$. We believe that δc is exponentially small, since the only way the droplet ‘knows about’ the boundaries is through the bulk correlation. Thus, the leading correction relevant to simulations is of order $1/L$. This forms the basis of the extrapolation of our Monte Carlo data.

4. Monte Carlo simulation

Simulating the Ising model on a square lattice using Kawasaki dynamics (Kawasaki 1972), we locate the (L -dependent) phase boundary $\bar{\phi}_c(T)$ by first performing a reverse temperature quench from $T=0$, either at fixed, small or large $\bar{\phi}$ (i.e. starting with either a compact droplet or a strip). After the system reaches equilibrium, the magnetization is changed in small steps at fixed T across $\bar{\phi}_c$. To define a quantitative measure of whether the system is in a strip or a droplet phase, we consider the structure factors $S_x \equiv S(k_x = 2\pi/L, k_y = 0)$ and $S_y \equiv S(k_x = 0, k_y = 2\pi/L)$. The droplet-strip transition can now be determined by studying the distribution function $P(\Delta S)$, where $\Delta S \equiv |S_x - S_y|$. In the droplet phase, P peaks about zero, while it peaks at a finite ΔS in the strip phase. The transition is identified as the point of equal peak heights.

Because of the long lifetimes of metastable states near $\bar{\phi}_c$, and slow dynamics at low T , our simulation is in practice limited to relatively small system sizes ($L \leq 40$) and high temperature ($T \geq 0.8T_c$). Despite these constraints, the transition is fairly well defined, and a linear extrapolation to the $L = \infty$ limit correctly reproduces the exact analytical values of $\bar{\phi}_c$ (figure 3). It is somewhat unfortunate, at these temperatures, that the exact results come so nearly isotropic that the extent and beauty of the anisotropic surface tension cannot be fully appreciated in our simulations.

5. Summary and outlook

We investigated the effects of boundary conditions and system geometry on equilibrium crystal shapes of Ising systems. A new class of transitions ‘inside the coexistence curve’, characterized by different cluster shapes is found. Their existence depends crucially on not only the conservation of total magnetization, but also periodic boundary conditions (across some edges). Since the anisotropic surface tension of the 2D Ising model on a square lattice is known exactly, we are able to locate the phase boundary for all temperatures below T_c , and show its explicit dependence on the anisotropy of the nearest neighbour couplings and the (rectangular) system geometries. We carried out Monte Carlo simulations on the isotropic, square system and confirm these predictions. We emphasize that these transitions survive the thermodynamic limit and we studied the leading corrections due to finite-size effects.

It is clear that the transitions we found depend on the *topology* of the system as well. For example, if our Ising model is realized on the surface of a sphere, then there would be no strips at all. The system will always phase separate into two droplets, i.e. regions with unity as its homotopy group. Although such a system may be difficult to simulate, since one cannot put a homogeneous lattice on a sphere, it is conceivable to study the liquid-gas system within the context of molecular dynamics (see e.g. Sikkenk

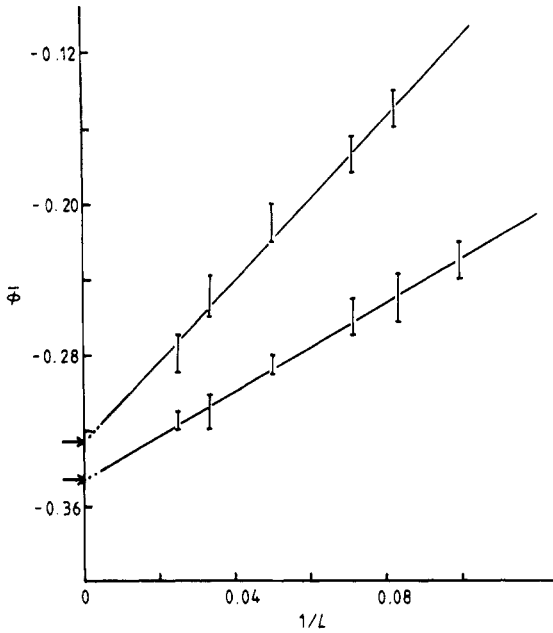


Figure 3. Linear extrapolations of the Monte Carlo data of the mean magnetization $\bar{\phi}_c(T, L)$ at the transition at temperatures (a) $T = 0.9T_c$ and (b) $0.8T_c$. The arrows indicate the exact results obtained in section 2.

et al 1987). Of course, the droplet will be uninterestingly circular in this case. At a more ‘academic’ level, we can pursue the issue further and investigate how these transitions will be affected if we impose other boundary conditions on the square lattice, such as shifted periodic and those corresponding to a Möbius band, a Klein bottle and the projective plane.

We end with some remarks concerning the first-order nature of these phase boundaries. Clearly, each configuration is a local minimum (of an appropriate coarse grained free energy functional). That is, an energy barrier exists between these local, degenerate minima at the transition point itself. Slightly beyond the transition, the configuration with the higher energy will be metastable. Following the usual line of study of first order transitions, we naturally ask about the ‘saddle point’, the energy of which will control the lifetime of the metastable states (Fisher 1967, Langer 1967). Far below criticality, it is sufficient to approximate the total free energy by only the surface term, i.e.

$$E[S] = \int_S da(\hat{n})\sigma(\hat{n}) \tag{5.1}$$

where the integral is taken over the interface S between the coexisting phases. If we were to seek the saddle point following the methods for bulk first-order transitions, we would look for a configuration S_0 which extremizes (5.1), i.e.

$$\left. \frac{\delta E}{\delta S} \right|_{S_0} = 0. \tag{5.2}$$

Of course, the solutions to this equation will include the minima (droplet and strip)

as well. The distinguishing feature of S_0 would be the existence of a *single* negative eigenvalue in the stability matrix $\delta^2 E / \delta S^2|_{S_0}$.

We believe that carrying out this program literally would fail for our case. In particular, we conjecture that S_0 is just a lens-shaped ‘pinched strip’ (see figure 4) with the interface meeting at a single point. Then, $E[S]$ is not analytic at this ‘saddle point’, so that, instead of satisfying (5.2), the first derivative is *discontinuous*. In pictorial terms, the energy functional resembles more like a knife-edged ridge there than a smooth saddle.

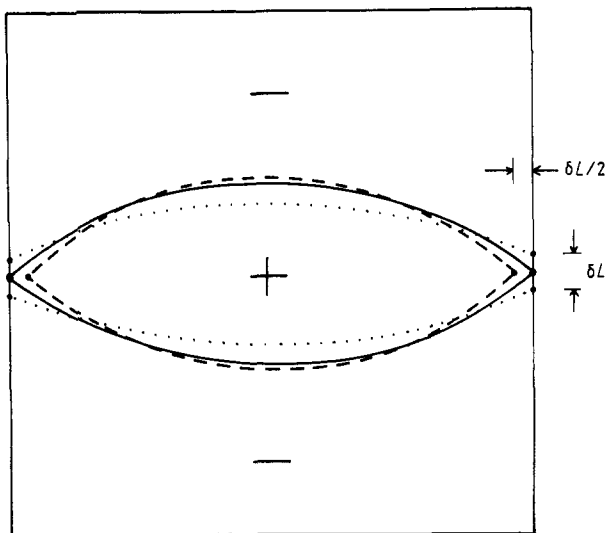


Figure 4. The proposed saddle point, characterized by interface shape S_0 (full curve), associated with the first-order droplet-strip transitions. Small deviations towards a droplet (broken curve) and a strip (dotted curve) are also shown.

To support our conjecture, we present some quantitative results for the case where the surface tension is isotropic and $f_c = 1/\pi$. Here, S_0 is composed of two arcs of a circle of radius R , which can be related to the volume of the droplet (L^2/π) and L via

$$\sin \theta = \frac{L}{2R}. \tag{5.3}$$

Note that 2θ is the angle of contact between the two arcs, satisfying the transcendental equation

$$\theta = \left(\frac{2}{\pi} \sin \theta + \cos \theta \right) \sin \theta. \tag{5.4}$$

Numerically, $\theta = 0.860(49.3^\circ)$. The ratio $E[S_0]/E[\text{strip}]$ is just $\theta/\sin \theta$, which is indeed greater than unity. The difference $E[S_0] - E[\text{strip}] = 0.135 E[\text{strip}]$ is the leading contribution to both the (essential) singularities associated with the droplet-strip transition, as well as the lifetime of metastable states near the transition.

To exhibit the nature of a saddle at S_0 , we investigate how E changes for small variations away from S_0 . If we hold the pinching point fixed, it is a standard calculation to show that small variations of the arc (which conserves the droplet volume) will lead

to a longer interface and a larger $E[S]$, at the *second*-order level. On the other hand, we may 'release' the pinched point (figure 4), so that, for example, the lens length is shorter than L by δL . Some simple algebra leads to

$$\frac{\delta E}{E} = -\frac{\delta L}{L} \frac{\sin \theta \cos \theta}{\theta} = -0.575 \frac{\delta L}{L}. \quad (5.5)$$

This equation supports our conjecture in that (a) the *first* variation does not vanish and (b) the energy *decreases* from $E[S_0]$.

A similar calculation can be done for releasing the pinched point so that the configuration is closer to the strip (see figure 4). Denoting the gap opened up at the pinched point by $\delta L'$, we find

$$\frac{\delta E}{E} = -\frac{\delta L'}{L} \frac{\sin^2 \theta}{\theta} = -0.668 \frac{\delta L'}{L} \quad (5.6)$$

thus supporting our claim of a ridge-shaped saddle at S_0 .

To summarize, we have shown that our saddle point has the novel feature that it does not satisfy the Euler-Lagrange equation. Although there is no reason to believe that the prefactor of the essential singularities associated with this transition will be significantly altered from the standard forms, we believe that this novelty deserves further studies.

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